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Newsletter

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## No. 239

## August, 1978

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DEADLINE DATES: No. 240: 11 September 1978 No. 241: 2 October 1978

All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro Department of Chemistry Texas A&M University College Station, TX 77843 U.S.A.

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<sup>239-1</sup>Dr. Vladimir Bystrov

USSR Academy of Sciences Shemyakin Institute

of Bioorganic Chemistry

Ul. Vavilova 32 Moscow 117312 USSR

June 28, 1978

Professor Bernard L.Shapiro Department of Chemistry College of Sciences Texas A & M University College Station, Texas 77843 U.S.A.

## <u>Title</u>: Selectively Spinlabeled Neurotoxin II

Dear Barry:

We concentrated our efforts on conformational study of neurotoxin II (NT II) from Central Asian cobra Naja naja oxiana whose letal activity arises from its ability to block transmission of the nerve impulse due to specific binding with the membrane acetylholine receptor. The microenvironment of the His-4, His-31, Tyr-24, Trp-27 ( and Trp-28 side chains were revealed in the native molecule (1 - 3). To obtaine further information on possible intramolecular interactions, which could shed light on the overall folding of the NT II, we made use of NMR reporter groups incorporated in the molecule.

Five monoacetylated NT-II derivatives were prepared with one acetyl group either at Lys-15, Lys-25, Lys-26, Lys-44, or Lys-46 residue. Trifluoroacetylation of these compounds and of native NT-II afforded the acetyl-pentatrifluoroacetyl- and hexatrifluoroacetyl derivatives, which were subjected to CD and <sup>1</sup>H- and <sup>19</sup>F-NMR studies. The availability of this series permitted complete assignment of the  $^{19}$ F signals (3,4). The above NT-II derivatives retain the overall conformational properties of the parent NT-II, as follows from the <sup>1</sup>H-NMR and CD spectra. Examination of the CD curves taken in aqueous media of various pH and in mixed trifluoroethanol-water solutions showed that the interactions between the amino groups and carboxyl groups contribute to the stability of the NT-II spatial structure. Comparison of the <sup>19</sup>F chemical shifts of the acetyl-pentatrifluoroacetyl derivatives indicated spatial proximity of the Lys-26 and Lys-46 side chains, while computer delineation of the pH-dependences

of the <sup>19</sup>F resonance positions provided the pK values of the proximate titratable groupings (3, 4). The different extent of <sup>19</sup>F signal broadening indicated that the exposure of the amino groups to the environment are in the following order of the amino acid residue: Lys-25 > Lys-26 > Lys-46 > Lys-15, Lys-44, Leu-1 (N-terminal) (3).

Recently we prepared two NT-II derivatives - one with the Lys-26 side chain containing trinitrophenyl group and the other a spin label. The former modification leads to shifts of a number of proton signals, and the latter to signal broadening. Calculation of paramagnetic relaxation (5) provided several inter-residue distances and allowed more detailed description to be given of the central fragment (loop II) of NT-II as shown below:



The conformational data thus obtained provide information on the sites essential for the biological action of NT-II, namely the loop II containing several invariant residues, such as Tyr-24,

239-2

Trp-28, His-31, Arg-32, Glu-37, and the Lys-26 and Lys-46 residues, whose modification leads to decrease of biological activity.

The NT-II derivatives described above, together with other spin and fluorescence labeled analogs now under preparation will be used to arrive at a more complete solution structure of NT-II and to study the neurotoxin-receptor interactions.

Sincerely yours,

Madimir

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References:

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- A.S.Arseniev, et al., Eur. J. Biochem. <u>71</u>, 595 (1976); Bioorgan. Khim. (USSR) <u>4</u>, 197 (1978).
- 3. V.F.Bystrov, et al., J. Magn. Res., in press.
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- 5. R.W.Wien, J.D.Morrisett, H.M.McConnell, Biochemistry 11, 3707 (1972).

GESELLSCHAFT ZUR FÖRDERUNG DER SPEKTROCHEMIE UND ANGEWANDTEN SPEKTROSKOPIE E. V. INSTITUT FÜR SPEKTROCHEMIE

### Postanschrift: Institut für Spektrochemie, 46 Dortmund, Postfach 778

Professor Bernard L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843

United States of America



46 DORTMUND, 28.6.1978 Bunsen-Kirchhoff-Str.11 (Abzweig Ardeystraße) Fernruf (0231) 129001-04

Betreff :

1

Making the JEOL FX-100 more flexible

Dear Professor Shapiro:

Some months ago I started to work at this Institute where, during the foregoing year, a JEOL FX-100 NMR-Spectrometer had been installed. Comparing this equipment to others I worked with previously, I must say that the quality of the obtained spectra is very good. For the measuring of routine spectra the software package delivered by JEOL is sufficient and the light pen procedures for parameter setting are very fast.

But having the experience with other FT-NMR-equipment that usually includes a teleprinter, I was sorry for not having an input-output device which during the NMR experiment, records experimental conditions and prints out the results. In my opinion the built-in column printer (output only) is merely a weak substitute for a teleprinter.

The more important reason why I missed a teleprinter was due to the fact that new software procedures can only be developed in an effective way when a teleprinter is used. Only by doing this, new experimental techniques and better data-handling procedures can be designed.

So I connected a Decwriter LA 36 to the built-in Texas 980 computer, using the intercommunication module from Texas Instruments. (By the way, the costs for the Decwriter and the module are jointly lower than the cost for the column printer built-in by JEOL).

So now I am ready to commence with developing new software routines and I would be glad if any other colleague using a JEOL Spectrometer with a Texas 980 computer would contact me in the event that he is also interested in new software procedures. Perhaps it would be possible to form a pool of new programs and, what might be more important, to exchange information about the data system of the JEOL Spectrometers.

I am convinced that by doing something in this field, the JEOL system may prove much more flexible than it is at present.

Sincerely yours, R. phis

239-4



EIDG. TECHNISCHE HOCHSCHULE ZÜRICH

> Laboratorium für Physikalische Chemie

> > Prof. Dr. R. R. Ernst

CH-8006 Zürich, June 29, 1978 Universitätstrasse 22 Tel. (01) 32 62 11

Prof. B.L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843 U S A

#### SCALING OF HETERONUCLEAR SPIN-SPIN COUPLING

Dear Barry,

In TAMU-letter 232 Ray Freeman and Gareth Morris have proposed a modified 2D spectroscopy experiment to obtain carbon-13 spectra with homogeneously scaled proton-carbon couplings as an alternative to off-resonance decoupling. Such a technique could become very useful for the analysis of complicated carbon-13 spectra.

We would like to propose here a further alternative with considerable advantages (and disadvantages) in comparison to the Freeman-Morris technique. Our method involves a simple 1D Fourier experiment, does not require any software modification and is as fast as any standard carbon-13 experiment.

Scaling of the heteronuclear couplings is obtained by applying a pulsed decoupling sequence to the protons and employing synchronized sampling of the carbon-13 FID in the following manner:



By varying the flip angle in the series of alternating  $\alpha$ and  $-\alpha$  pulses, it is possible to obtain arbitrary scaling factors. The dependence on frequency offset can be minimized by optimizing pulse amplitude and pulse length.

Two examples of scaled spectra of propionic acid ethyl ester together with the unscaled spectrum are shown in the figure. The additional lines near 29 ppm originate from the acetone-d<sub>6</sub> solvent. Indeed a homogeneous scaling has been achieved. But at the same time, it is apparent that the outer multiplet lines become weaker upon scaling. This is not only due to rf field inhomogeneity but mainly to the increased effects of strong proton-proton coupling. The proton chemical shifts are scaled as well but proton-proton couplings remain invariant. Therefore, scaling leads to a more tightly coupled proton-spin system which causes a complicated splitting pattern in the carbon-13 spectrum. This is an effect which occurs also in offresonance decoupling.

Nevertheless, we feel that the experimental simplicity of this technique makes it quite useful for practical applications.

Sincerely yours

W. P. aue

licharl

239-6

W.P. Aue

R.R. Ernst



Baylor College of Medicine NATIONAL HEART AND BLOOD VESSEL RESEARCH AND DEMONSTRATION CENTER Department of Medicine 713/790-5826



\* 239-8

July 5, 1978

Dr. B. L. Shapiro Department of Chemistry Texas A&M University College Station, Texas 77843

## Two Years After the Flood

Dear Professor Shapiro:

June 15 was the second anniversary of our underwater NMR. There are several quirks in the system but I do not believe the following are related to submersion in a meter of muddy water.

### Linear Field Gradient

Seems I have a 3.7 mGa/mm linear (over 20 mm) gradient in my XL 100-15 magnet with the hom. coils disconnected. There are no thermal gradients in the magnet coils. The fix according to a qualified manufacturer's representative is to reshim the magnet. Won't someone tell me the likeliest source of this gradient so that I can avoid the same mistake in the future?

## Noise Suppression Via A.P.R.

I have known for some time that there is a slight difference in the distance top to bottom from the pen carriage to the platen in my recorder. Fortunately, the pen is closer at the bottom of the platen. This slightly greater pressure causes a little more pen friction in the noisy baseline and fortuitously less response (call this Attenuated Pen Response). The A.P.R. seems to be linear but has not been quantitated since I only recently realized how lucky (?) that the effect was not reversed.

Sincerely intended,

Roger D. Knapp, Ph.D.

Instructor in Experimental Medicine

RDK/dm



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE PUBLIC HEALTH SERVICE NATIONAL INSTITUTES OF HEALTH BETHESDA, MARYLAND 20014

July 13, 1978

Building 2, Room B2-08

Professor B. Shapiro Chemistry Department Texas A&M University College Station, Texas 77843

Title: Calibration of Internal pH by <sup>31</sup>P NMR

Dear Barry:

In order to calibrate the ATP signals obtained from chromaffin granules as a function of pH, we have reversibly adjusted the internal pH of granules to different values by three methods which equalize the internal and external pH values. Using this approach, the complete titration curve of the terminal phosphate (P) of <u>intragranular</u> ATP was measured by NMR between pH 3 and 8 (Figure).

This titration curve was quite different from the simple curves of either Na<sup>+</sup>, Ca<sup>2+</sup>, or Mg<sup>2+</sup> ATP in solution, or of ATP in a physiologically stoichiometric mixture of granule lysate proteins, epinephrine, calcium and magnesium. Instead, the curve of intragranular ATP had two inflections of relative proportions ca. 1:2 with  $pK_a$  values 6.4 and 4.3, corresponding to the titrations of P $\gamma$  and the purine ring, respectively. In addition, the P $\gamma$  resonance of intragranular ATP was shifted downfield by 2.2 ppm at the intragranular pH. The P $\gamma$  atom of internal ATP may experience the titration of the adenine ring and the deshielding as a result of a close coplanar juxtaposition with the purine ring. Such a conformation is found in crystalline ATP, but apparently not in free solution.

Using the new calibration curve, we found that the intragranular pH was 5.7, a value consistent with independent methods, and that exposure of the granule to external MgATP caused the intragranular pH to decline to 5.4. We also computed from the titration curve of internal ATP that the internal pH was at a point at which ca. 95% of the P $\gamma$  was protonated to its singly ionized form and 95% of the ring nitrogens were unprotonated in the neutral form, leaving ATP with a minimum net charge. This presumably aids in the packaging of high concentrations of ATP into the granules, and may relate to the pH-dependence of granule function.

Previous attempts to quantitate internal pH from ATP-P $\gamma$  have been based on the explicit assumption that the titration curves of ATP in free solution and in granules were identical. We have shown that this is not the case and we would expect future studies of this kind to incorporate an in situ calibration similar to that described here. Professor B. Shapiro

July 13, 1978

This work will be presented at the International Biophysics Congress in Kyoto in September (H. Pollard, H. Shindo and J. S. Cohen) and will be the subject of a forthcoming paper.

Yours sincerely,

Jack S. Cohen Developmental Pharmacology Branch National Institute of Child Health and Human Development

JSC:e11

Figure. Composite titration data of intragranular ATP-P $\gamma$  chemical shift as a function of internal pH. The theoretical curves are best fits with one (----) and two (----) components (see Table I for parameters); for comparison, a one component fit (----) with the same extreme chemical shift values as the two component fit is given. The RMS errors for these three fits to the granule titration data are 0.35, 0.19 and 0.59, respectively, confirming that the data is best fit by a two component curve.



C:

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14th July, 1978

RF/EP

Professor Bernard L. Shapiro, Dept. of Chemistry, Texas A and M University, College Station, Texas, U.S.A.

Dear Barry,

### "Fourth European Experimental NMR Conference"

Newsletter readers might be interested to know the date and venue of the next E.E.N.C. meeting. This will be held June 26 - June 29th 1979 in the "Olympic Village" at Autrans near Grenoble, France. Participants at the Third E.E.N.C. in Elsinore, Denmark will automatically receive the first circular about this meeting, but other interested readers should contact the local arrangements chairman, Dr Pierre Servoz-Gavin, Centre d'Etudes Nucléaires de Grenoble, 38041 Grenoble Cedex, France. The program will consist of invited lectures and poster sessions; a small number of the latter will be "promoted" to contributed papers. The preliminary scientific program will include:

Very High Field NMR Two-Dimensional Fourier Transformation Spin Mapping Solid State NMR Polymer Studies Anisotropy of NMR Parameters Relaxation Techniques in Biochemistry Multiple Quantum Transitions Liquid Crystals

The general theme will emphasize new techniques rather than new applications.

Kindest regards,

Ray



#### UNITED STATES ENVIRONMENTAL PROTECTION AGENCY HEALTH EFFECTS RESEARCH LABORATORY RESEARCH TRIANGLE PARK NOR TH CAROLINA 27711

July 7, 1978

Dr. Bernard L. Shapiro Department of Chemistry Texas A&M University College Station, Texas 77843

Gem-Diol Hydrogen Bonding and Structure of Kepone Photoproducts

Dear Barry:

We have been involved in <sup>1</sup>H and <sup>13</sup>C nmr characterization of the chlorinated pesticide Kepone<sup>1</sup> and some of its derivatives and photoproducts. In solution Kepone is usually in the gem-diol form (1). Carefully dried samples of the monohydrophotoproduct (2) show separate signals for the two magnetically non-equivalent geminal hydroxyl protons as in Figure 1. These signals do not coalesce with increased temperature, thus the OH protons do not participate in intramolecular exchange. They do show a very strong temperature dependence as shown in the figure, which we attribute to a monomer-dimer equilibrium involving the dimer (3). Unfortunately, proton exchange also occurs with traces of water in the samples, and further investigations of this interesting hydrogen bonding system have been thwarted by difficulties with reproducibility. The diol water itself is loosely held, since it comes off at 130°C to give the carbonyl form (4).

In this same series of compounds, we have isolated the dihydrophotoproduct of Kepone for the first time, and have determined its structure unequivocally. The mass spectrum gives a choice of (5) or (6) for the structure of dihydrokepone, but since these differ in symmetry, the six resonances in the <sup>13</sup>C spectrum show immediately that the correct structure is (5).

This work has been done in collaboration with Robert D. Zehr of this laboratory. Carbon-13 studies of the complete series of compounds should appear in the literature soon.

With best wishes.

Sincerely yours,

Náncy K. Wilson Methods Development Section Analytical Chemistry Branch (MD-69)













(2)









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NMR STUDY OF PRODUCTS OF VILSMEIER FORMYLATION OF PHOSPHAFERROCENES

Phosphaferrocenes (1,2) are together with phosphocymantrenes<sup>(3)</sup> the only know carbon-phosphorus heterocycles with a true "aromatic" chemistry : they undergo typical electrophilic substitutions such as Friedel Crafts acylation. In fact, however, phosphacymantrenes are not prone to such reactions and we have failed when attempting alkylations or formylation of 3,4 dimethyl phosphacymantrene. On the other hand, the situation is much more favourable with phosphaferrocenes ; we have succeded when attempting a Vilsmeier formylation of 3,4 dimethylphosphaferrocene :



Since only the most aromatic substrates are prone to such a formylation, this success means that phosphaferrocenes are highly "aromatic" species. A lot of interesting fonctional derivatives can probably be synthesized starting with this aldehyde. The full comparison of the <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra of 3,4 - dimethylphosphaferrocene and its 2- formyl derivatives is presented hereafter:



<sup>1</sup> H (CDC1 <sub>2</sub> , intern	al TMS)		
Me	2.17	2.18	2.41
СН (Ј(Н-Р))	3.71 (36)	4.20	(36)
C <sub>5</sub> H <sub>5</sub>	4.13	4.20	
СНО (Ј(Н-Р))	-	9.81	(4.4)

13<sub>C</sub> (CDC1<sub>3</sub>, TMS)

Me	16.4	14.3	16.4
$C_{\chi}$ (J(C-P))	78.2 (61)	83.0 (59.6)	88.2 (57.3)
С <sub>в</sub> (Ј(С-Р))	94.8 (7.2)	94.5 ( 4.5)	101.1 (8.1)
с′ <sub>5</sub> н <sub>5</sub>	71.4	73.0	
CHO(J(C-P))	_	196.5	(28)

 $31_{P}$  (CDC1<sub>3</sub>, external  $P_4O_6$ )196 174.4  $\int$  + for upfield shift

The detection of the carbon bearing the CHO substituent  $(\delta^{13}C = 88.2)$  needs the addition of Cr(Acac)<sub>3</sub> to the solution of the aldehyde.

R. MANKOWSKI F. MATHEY G. MAVEL

## GRIFFITH UNIVERSITY



239-21

Nathan, Brisbane, Queensland, 4111. Telephone (07) 275 7111. Telegrams Unigriff Brisbane

School of Science Chairman: Dr. D. M. Doddrell Ref:

Professor B.L. Shapiro, Department of Chemistry, Texas A & M University, College Station, TEXAS 77843, U.S.A. 20th July, 1978.

Dear Professor Shapiro,

## Variable Frequency <sup>13</sup>C Studies on a Multinuclear HX-90

We have recently set up our multinuclear HX-90 (18" magnet) to run  ${}^{13}$ C at 10.8 MHz by locking to external "B at 13.8 MHz with proton decoupling at 43.1 MHz, thus enabling us to perform variable frequency  ${}^{13}$ C experiments on one spectrometer. The only disadvantages compared with normal 22.6 MHz operation are the loss of signal to noise (~4) and having to shim on the FID. As an example of what we are able to do, we have confirmed the frequency dependence of the  ${}^{13}$ C T<sub>1</sub>'s of 1,2 decanediol found by Levy et al.1'2 At 57°C for a neat sample, we found a similar field dependence (Average decrease of T<sub>1</sub> of C<sub>1-9</sub> is 34%, S.D 5.3%) and propagation of the effect through the ten carbon chain. Levy<sup>2</sup> found a dependence over the range 30°C-65°C, whilst we repeated the measurements at the higher temperature of 85°C and found no observable dependence (preliminary result as experiment yet to be repeated).

Table:  $T_1$ 's for 1,2 decanediol at 22.6 and 10.8 MHz

	-	1	2	3	4	5	6	7	8	9	10
22.6	MHz										
	57 <sup>0</sup> C	.52	.72	.43	.49	.59	.73	.88	1.26	2.01	3.77
	85 <sup>0</sup> C	.96	1.41	.84	1.00	1.10	1.31	1.67	2.53	3.74	6.24
10.8	MHz										
	57 <sup>0</sup> C	.31	.44	.28	.34	•	46*		.94	1.48	3.46
	85 <sup>0</sup> C	1.18	1.63	1.93	1.15	1.	68*		2.25	3.53	~6.0
* A	verage T <sub>1</sub> fc	or $C_{5,6}$	,7								
(1)	C C 1 0000	MD	Condoc	1 0	Lowic	and D			1 Am Ch		

(1) G.C. Levy, M.P. Cordes, J.S. Lewis and D.E. Axelson <u>J.Am.Chem.Soc.</u>, <u>99</u>, 5492 (1977)

(2) G.C. Levy, M.P. Cordes and D.E. Axelson, TAMUNMR 234-7

D.M. Doddrell	$\Lambda$	P. Barron	<u>J. Fijeld</u>
M. Dallelm	L.	(Buron	A mos hits.

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DEPARTMENT OF BIOCHEMISTRY



THE UNIVERSITY OF ALBERTA EDMONTON, CANADA T6G 2H7

PHONE: (403) 432

July 13, 1978

Professor Bernard L. Shapiro, Department of Chemistry, Texas A & M University College Station, Texas, U.S.A. 77843.

Dear Barry

## 10 mm <sup>19</sup>F Probes at 254 MHz

Recently we have been interested in using 10 mm sample tubes for  $^{19}$ F NMR on our Bruker HX-270. This does not seem so adventurous given that people are using 20 mm and larger tubes for several nuclei. What we found, as could have been expected, was that the homogeneity requirements are much more stringent for  $^{19}$ F. With the high magnetogyric ratio, a given field in homogeneity  $\Delta H$  is much larger when expressed in frequency units  $\Delta v = \gamma \Delta H$ . To make matters worse we also always restrict ourselves to short samples so as not to use large volumes of biological materials and this does not help matters.

Our first attempt involved retuning the <sup>1</sup>H decoupling coils on our 10 mm <sup>31</sup>P probe to resonate at 254 MHz. With this setup we first observed how bad the field homogeneity could look for <sup>19</sup>F when the field looked well tuned for <sup>31</sup>P. When we then tuned it up on <sup>19</sup>F, it was better but not overwhelmingly so for <sup>31</sup>P. The major problem with this setup since the signal to noise was reasonable was a large fairly narrow <sup>19</sup>F background. Nevertheless, we were able to use it for combined <sup>19</sup>F/ <sup>31</sup>P NMR studies of the interaction of 2-fluoro ATP with myosin.

We are presently making our own <sup>19</sup>F probes with good success. The major remaining problem is the <sup>19</sup>F signal from the Teflon vortex plugs.

Best Regards,

John H. Baldo

Gerry McQuaid

Gerrynchiad

Brian D. Sykes



Stauffer Chemical Company

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## July 18, 1978

Professor B. L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843

Dear Barry:

## Carbon-13 NMR Studies of Oxazolidines and Schiff Bases

Oxazolidines and Schiff bases are known to be in mobile equilibrium (1). Although proton NMR has been applied to study the equilibrium between oxazolidines and Schiff bases (2), it is rather difficult to obtain important parameters from proton NMR spectra due to the overlapping of peaks. Because of its wide range of chemical shifts, carbon-13 NMR offers an ideal method to study this type of equilibrium. We have studied the reaction products of ethanolamine and ketones of the type  $CH_2C(0)R$  where R is methyl, ethyl, isopropyl, and t-butyl. When R is other than a methyl group, the Schiff base in the product is expected to have the E- and R- forms. This is indeed observed when R is an ethyl group. The ratio of oxazolidine, Eand Z- Schiff bases is approximately 67:26:7 in neat solution, However, when R is an isopropyl or a t-butyl group, only the E- form is observed in addition to its corresponding oxazolidine. The carbon chemical shifts of various oxazolidines and Schiff bases are listed in the table.

Sincerely yours,

**References:** 

1. E. D. Bergmann, Chem. Rev., 53, 309 (1953).

2. J. V. Pauketelis and R. M. Hammaker, Tet. Letters, 3557 (1968).

		Oxaz	olidine	S	Schiff Bas	se (E-form	n)	
<u>R</u>	Me	Et	<u>i-Pr</u>	<u>t-Bu</u>	Me	Et	i-Pr	t-Bu
C-1		8.96	17.96; 18.25	25.64		10.91	19.82	27.70
C-2	26.22	32.08	36.42	38.17	28.76	35.44	39.95	40.45
C-3	26.22	23.66	20.38	20.87	18.89	17.18	14.74	13.77
C-4	94.72	97.03	99.42	100.94	168.89	172.64	175.90	176.76
C-5	45.89	45.91	46.09	46.38	53.94	53.80	53.50	52.79
C-6	65.04	65.14	65.32	66.03	61.63	61.90	62.02	62.26

Carbon-13 Chemical Shifts<sup>1</sup> of Oxazolidines<sup>2</sup> and Schiff Bases

1. Chemical shifts, expressed in ppm from TMS, were measured (50% by volume in  ${\rm CDCl}_3$ .

2.







TUCSON, ARIZONA 85721

COLLEGE OF LIBERAL ARTS DEPARTMENT OF CHEMISTRY

July 18, 1978

Professor Bernard L. Shapiro TAMU NMR Newsletter Department of Chemistry Texas A&M University College Station, TX 77843

Dear Barry:

RE: THE γ-METHYL EFFECT ON VICINAL COUPLING WITH <sup>13</sup>C

The  $\gamma$ -effect on <sup>13</sup>C chemical shielding is well-known, but I am not aware that there have been any previous reports showing that  $\gamma$ -methyl or methylene substituents on C3 decrease the magnitude of the vicinal <sup>13</sup>C coupling constant [<sup>3</sup>JCX(180°)] between the C1 carbon and the trans oriented nuclear spin X. Previously, it was noted (1) that INDO-FPT MO results for <sup>3</sup>J<sub>CC</sub>(180°) in the series trans-butane, equatorial methylcyclohexane,

and 1-methyladamantane were 4.27 Hz, 3.72 Hz, and 3.32 Hz, respectively, and it was proposed (1) that the decrease paralleled the increase in the number of carbon rear lobes impinging in the center of the cyclic structures. More recently, it was suggested (2) that the calculated decrease correlated with the increase in the number of  $\beta$ -methylene substituents. From recent experimental data obtained in collaboration with Jim Marshall and Bob Willcott, and a large number of calculations, including the ones in the table, it is now clear that these are  $\gamma$ substituent effects arising from the 1,4-type interactions. For the case of vicinal C-C coupling this would not be apparent because a  $\beta$ -substituent is also a  $\gamma$ - to a carbon.

The results for  ${}^{3}J_{CH}$  in Table I clearly indicate that the effects of  $\beta$ -methyl groups are small in comparison with  $\gamma$ -methyls, and for the series of cyclic molecules having a single  $\gamma$ -methylene  $\Re - \Im _{3}J_{CH}$  is decreased by 1.2-1.4 Hz, where-as with two  $\gamma$ -methylenes 12 and 13, the decrease is 1.8 to 2.0 Hz. The experimental results in the series propane, cyclohexane, and adamantane suggest that the actual  $\gamma$ -effects is at least twice as large as the calculated.

To sort out the various interactions, a modified INDO-FPT procedure was adopted wherein selected elements of the Fock Matrices were set equal to zero in each SCF cycle, thereby eliminating that interaction as a possible coupling path. For example, in the calculation of  ${}^{3}J_{CH}$  for 2-methylbutane 8, the most important substituent interactions (-2.65 Hz) is that involving the hydrogen atoms on C1 and the six hydrogen atoms of the two  $\gamma$ -methyls. This is partially offset by the next-most important contribution (+1.24 Hz) arising from interactions from the valence atomic orbitals on the C1 carbon atoms and the hydrogens of the two  $\gamma$ methyls.

There are a number of other examples where the recognition of a substituent  $\gamma$ -methyl effect would remove apparent anomalies.

- M. Barfield, S. A. Conn, J. L. Marshall, and D. E. Miller, J. Am. Chem. Soc., 98, 6253 (1976).
- (2) V. Wray, <u>ibid</u>., <u>100</u>, 768 (1978).

Sincerely yours,

Mike Barfield

Table I. INDO-FPT results for trans vicinal coupling constants  $[{}^{3}J_{CH}(180^{\circ}), {}^{3}J_{CC}(180^{\circ}), \text{ and } {}^{3}J_{CF}(180^{\circ})]$  in propane (X = H), butane (X =  ${}^{13}CH_{3}$ ), and fluoropropane (X =  ${}^{19}F$ ), as well as methyl-substituted and cyclic compounds exhibiting these types of coupling. Experimental values are in parentheses.<sup>a</sup>

	Molecule	<sup>3</sup> J <sub>CH</sub>	<sup>3</sup> J <sub>CC</sub>	<sup>3</sup> J_CF	Mol	ecule 3	<u>Ј</u> СН	<sup>3</sup> J <sub>CC</sub>	<sup>3</sup> J <sub>CF</sub>
2	*CCX	8.78 (13±1)	4.27	23.71	92 2	*CX 7 X (8	.63 .12)	3.72	17.38
32	*C _ C _ X	8.74	4.26	24.03	10 *C-	X 7	.57	3.33 <sup>d</sup> (3.44)	15.39
4 2	*c c x	8.62	4.12	21.33		2			
52	*CCX	8.72	3.81	21.36	11 <sup>*C</sup>	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	.35	-	16.29 (9.8)
Ŕ	*CCX	8.74	3.44	19.24	12 × C	X 6	.96	3.39	14.13 (11.5)
7	*CCX	7.82	3.81	18.84	13	6 (5	.82 .33)	3.33 (3.2)	13.08 (9.61)
82	*CX	7.07	3.44	15.02	*C	x			

<sup>a</sup>All values in hertz. Experimental values from this and other studies are given in parentheses.

## UNIVERSITY COLLEGE OF SWANSEA



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J. H. Beynon, D.Sc., C.Chem., F.Inst.P., F.R.I.C. F.R.S., Royal Society Research Professor.

26thJuly 1978

J. H. Purnell M.A., Ph.D., Sc.D., C.Chem., F.R.I.C. Professor of Physical Chemistry and Head of Department. A. Pelter Ph.D., D.Sc., D.C.C., C.Chem., F.R.I.C. Professor of Organic Chemistry.

Professor B.L. Shapiro Department of Chemistry Texas A and M University College Station Texas 77843 U.S.A.

<u>Title:</u> "C NMR Spectra of Methyl Substituted Fulgides"

Dear Professor Shapiro,

In an attempt to assess the effect of induced ring currents on carbon nuclei we have recorded the  $^{13}$ C n.m.r. spectra of a series of methyl substituted fulgides (1-14). The results are somewhat conflicting and may be of interest to your other readers.

The chemical shifts of the olefinic methyl groups are shown in the accompanying Table. We were particularly interested to compare the chemical shifts of the methyl groups in compounds of type A and B which differ in their configuration of the arylidene group.

Me Ar Ar Ar B

The comparisons of interest are underlined in the Table. Thus, comparing the chemical shifts of the  $\mathbb{R}^2$  methyl groups in compounds 2 and 5 with those in 3 and 6 reveals upfield shifts of 0.93 and 0.71 p.p.m., which can be attributed to the effect of the overlying aryl groups in 3 and 6. Furthermore the shifts are similar in magnitude to that observed in the spectrum of [12]-paracyclophane.<sup>1</sup> In contrast however, comparison of the signals due to the  $\mathbb{R}^2$  methyl groups in compounds 8, 10 and 12 with those in 9, 11 and 13 reveals downfield shifts of 0.64, 1.54 and 1.80 p.p.m. Since changing the configuration of the arylidene group causes significant changes in the chemical shifts of other carbon atoms, we conclude that the effect of the induced ring currents in compounds 9, 11 and 13 must be overshadowed by other effects resulting from the change of stereochemistry.

1. R.H. Levin and J.D. Roberts, Tetrahedron Letters, 1973, 135.

		Ra					239	-30
		R <sup>3</sup>		,				
		Í						
1.	$R^{1}=R^{2}=R^{2}$	$3 = R^4 = Me$	8	$R^1 = R^2$	=Me, R <sup>3</sup> =H	I, R <sup>4</sup> =mes	ityl	
2.	$R^{1}=R^{2}=R^{2}$	$^{3}$ = Me, R <sup>4</sup> =	Ph 9	• $R^{1}=R^{2}$	=Me, R <sup>3</sup> =r	ne <b>sityl,</b> R	<sup>4</sup> =H	
3.	$R^{1}=R^{2}=R^{2}$	$4 = Me, R^3 = 1$	Ph 10	$R^{1} = R^{2}$	$=R^3 = Me, I$	$4^{=\beta-naph}$	thyl	
4.	$R^{1}=R^{2}=M$	$[e, R^3 = R^4 = ]$	Ph 11	$\mathbf{R}^{1} = \mathbf{R}^{2}$	=Me, $R^3$ = $\beta$	-naphthy	<b>,</b> R <sup>4</sup> =H	
5.	$R^1 = R^4 = P^2$	$h, R^2 = R^3 = 1$	Me 12	$R^{1} = R^{4}$	=Ph, R <sup>2</sup> =N	$Ae, R^3 = H$		
6.	$R^{\dagger}=R^{\dagger}=P^{\dagger}$	h, R <sup>2</sup> = R <sup>4</sup> = ]	Me 13	$\cdot R^{1}=R^{3}$	=Ph,R <sup>2</sup> =M	[e, R <sup>⁻</sup> =H		
7.	R <sup>*</sup> =R <sup>*</sup> =M	le, R <sup>-</sup> =R <sup>-</sup> =	Ph 14	$\mathbf{R}^{T} = \mathbf{M} \mathbf{e}$	e, R <sup>″</sup> =R <sup>″</sup> =I	Ph, R <sup>*</sup> =H		
	Table.	<sup>13</sup> C	chemical	l shifts of	f methyl g	roups		
			Compo	und				
	<u>  1</u>	2	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	7	
R	22.18	22.36	22,55	22.76	-	-	22.76	
$R^2$	26.87	26.88	25.95	26.34	26.95	26.24	- 1	
R	26.87	26.88	-	-	26.95 	-	-	
R <sup>4</sup>	22.18		22,55	-	ı –	22.66	22.76	
			Compo	und				
1	<u>8</u> .	9	$\frac{10}{10}$	<u>11</u>	1 <u>12</u> 1	<u>13</u>	<u>14</u>	
R _ 2	124.55	23.62	22.45	23.00	I –	-	23.28 <sub>1</sub>	
R _ 3	25.88	26.52	26.89	28.43	26.34	28,14		
R 4	+ -   _	-	26,89	-	1	-	- 1 	
R	-	-	ı -	-	-	-	- 1	

\* all spectra recorded in  $CDCl_3$  solution.

Yours sincerely,

RS Ward.

R.S. Ward (University College of Swansea) H. G. Heller

H.G. Heller (University College of Wales, Aberystwyth)



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File Référence

## 28 July 1978

Professor B. L. Shapiro, Department of Chemistry, Texas A & M University, College State, Texas 77843, U. S. A.

Dear Barry:

## QUADRUPOLE ECHOES ON AN XL-100: A BOON FOR LIQUID CRYSTAL FANATICS

Last year in TAMU 228, 102 (1977) we reported on a major reconstruction project for our XL-100 to facilitate the observation of nuclei with large spectral dispersions and short  $T_2$  values. During the past year, this project has been completed and the system performance has been optimized. For our next contribution we hope to provide details of the spectrometer system. It works very well now, but our documentation is incomplete. This time we would like to tell you about quadrupole echoes observed on this instrument, and how they have facilitated the study of liquid crystals by <sup>2</sup>H NMR.

A major problem in the use of high resolution spectrometers to observe resonances of quadrupolar nuclei is that the free induction signal decays in a time comparable to or less than the ring down time of the probe and receiver. In high resolution work "pulse breakthrough" and wobbly baselines are minimized by a finite delay ( $\alpha$ -delay) between the pulse and commencement of data acquisition. On the XL-100 the built-in  $\alpha$ -delay is 50 µsec. In our type of system, <sup>2</sup>H NMR of quadrupolar powder patterns due to oriented lipids in membranes (1), we lose a large fraction of our signal intensity during this delay, and have great difficulty with phasing due to loss of early data points. These problems are largely circumvented by the quadrupole echo technique (2), a modification of the solid echo method (3) used for a system of two spin 1/2 nuclei with a residual dipolar coupling.

The echo is obtained using a pulse sequence  $90^{\circ}_{\circ}-\tau-90^{\circ}_{\circ}-\tau-Echo$ ; the trailing edge of the echo is acquired and Fourier-transformed. To gain  $\sqrt{2}$  in S/N and reduce power and spectral width requirements, we pulse on resonance, and therefore fold one-half of the symmetrical powder pattern onto the other. The resulting data may be plotted such as to reflect the half-spectrum about the offset frequency and thus yield a "complete" powder lineshape. We currently use a delay between 90° pulses of about 50 µsec;

28 July 1978

it can be longer but at the expense of S/N in the echo. The only tricky part of the whole business is adjusting the rf phase such that we obtain the maximum echo amplitude as the first data point of the acquisition - this minimizes any phase corrections. The figure shows such a spectrum obtained from 70% potassium palmitate- $d_{31}$ -30% H<sub>2</sub>O, a lyotropic liquid crystal. The various quadrupole doublets are due to the variation in order parameter with position in the chain (2,4). By using the quadrupole echo technique true intensity and lineshape information is obtained in contrast to the distortions observed from a simple free induction decay experiment.

It should be pointed out that the quadrupole or solid echo techniques only work when the system has a residual anisotropic interaction (dipole-dipole for two spin 1/2; quadrupole for spin >1/2).

We are very grateful to Professor Myer Bloom and Dr. Jim Davis of the Department of Physics, University of British Columbia, Vancouver, for introducing us to and advising us on this method.

Last but not least, we are happy to announce the forthcoming delivery (October) of a Bruker wide bore CXP-300 system equipped with multinuclear high resolution, broad line, cross-polarization, and magic angle spinning capabilities.

Yours sincerely,

RAB

R. Andrew Byrd

Ian C. P. Smith

LAT

Leo A. Turner

- I.C.P. Smith, G.W. Stockton, A.P. Tulloch, C.F. Polnaszek, and K.G. Johnson, J. Colloid and Interface Sci. <u>58</u>, 439 (1977).
- (2) J.H. Davis, K.R. Jeffrey, M. Bloom, M.I. Valic, and T.P. Higgs, Chem. Phys. Letts. <u>42</u>, 390 (1976).
- (3) P. Mansfield, Physical Review, <u>137</u>, A961 (1965).
- (4) B. Mely, J. Charvolin, and P. Keller, Chem. Phys. Lipids <u>15</u>, 161 (1975).



Deuterium NMR spectrum (15.4 MHz) of the potassium palmitate-water system (2) recorded from a 12 mm tube at <u>ca</u>.  $42^{\circ}$ C using 100 accumulated quadrupole echoes and 30 Hz line broadening. The total plotted spectral width is 50 KHz.

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01.08.1978/dd

Professor Barry L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843

#### HOW TO GIVE AWAY YOUR CAT

Dear Professor Shapiro,

The VARIAN C-1024 CAT was a widely used type of multi channel analyzer for signal-to noise ratio improvement before the introduction of the pulsed Fourier technique in nmr. For some years these instruments have remained unused in many laboratories. The improvement of S/N ratio is also a problem which may appear in mass spectrometry. Possible examples are:

- 1. Precise mass measurement of signals with weak intensity by peak-matching.
- 2. Detection of metastable spectra and of collision-activated spectra.
- 3. Analysis of the isotopic pattern.
- 4. Quantitative estimations.

We wish to show, how the nmr-spectroscopist may help in a simple way to solve such ms problems by connecting his CAT to the mass spectrometer.

Analysis of the Isotopic Pattern

Accumulated low resolution field desorption mass spectrum of a corrin-metalcomplex ( $C_{52}H_{72}BrCl_2N_4O_{16}Rh$ ). Experimental and calculated pattern of the molecular ion. In this case the analysis of the isotopic pattern gave an important indication for the correct interpretation of the high resolution data obtained by field desorption and photographic detection (M.W. 1260.256).

Mass spectrometer VARIAN MAT 731, Bremen.

The VARIAN C-1024 CAT was directed by the cyclic magnetic scan of the mass spectrometer.



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Fig. 1 Analysis of the Isotopic Pattern



Fig. 2 Quantitative Estimation of 5'-Methylcytosine in DNA

Quantitative Estimation of 5'-Methylcytosine in DNA

Accumulated high resolution electron impact mass spectrum of thymine and 5'methylcytosine of trifluoroacetic acid-treated rat liver DNA. Experimental conditions are given in the diagram inset. The evaluation of the peak area for thymine and 5'-methylcytosine yields without any correction an amount of 9.12 % of 5'-methylcytosine related to thymine.

Mass spectrometer MS 902 AEI, Manchester.

The interconnection between the mass spectrometer and the VARIAN C-1024 CAT was realized in the x-axis by use of a power amplifier whose output was directed to the auxiliary magnet coil of the spectrometer and controlled by the ramp of the CAT. The y-signal was fed to the CAT from the recorder amplifier of the spectrometer.

At present, the disadventage of this method for guantitative estimation is determined by the VARIAN C-1024. Because it is not possible to accumulate the signals for the two nucleobases in the two separately controllable areas of the CAT, both peaks must be produced close together. Thus a partial overlap of peaks is not avoidable which leads to difficulties in the evaluation of the peak areas a problem which can only be solved by an appropriate computer program. We are attempting to solve the problem of separate accumulation and we hope to simplify the evaluation considerably.

The advantage of a multi-channel-analyzer in relation to an accumulative registration by a data system exists in a direct visual control of all individual runs of all previously accumulated signals.

We hope, that this contribution will help to reactivate the use of many unused CATs.

1 V. Muilan (H. Stegemann)<sup>1</sup>

C.S.C.

L'haljadan

U.M. Leul

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239-39 Dr. Alois Steigel Institut für Organische Chemie der Universität Düsseldorf Direktor: Professor Dr. L. Birkofer

4 Düsseldorf, den July 27, 1978 Universitätsstraße 1 Fernsprecher 311-2298/99

Professor B. L. Shapiro Department of Chemistry Texas A and M University College Station, Texas 77843

Stereoisomeric Spiro Compounds

Dear Professor Shapiro,

In a collaborative study with the Fragrance Laboratories of Henkel in Düsseldorf we synthesized and characterized a series of spirodioxanes of type I. Although the compounds I,  $R = CH(CH_3)_2$  (1) and R = $CH=CH_2$ ,  $CH=CH-CH_3$  (2) have been described before, the latter forming the basis of numerous patents on epoxy resins, there was no mention of a stereoisomerism. By analysis of the <sup>1</sup>H NMR spectra we established that the 3-substituted 2,4-dioxaspiro(5.5)undec-8-enes are generally obtained as 1:1 mixtures of two isomers, which we separated by distillation in the case of  $R = CH_2$ .



The <sup>1</sup>H NMR spectra of the isomers IIa and IIb are shown in the Figure. The structural assignment can be easily achieved by comparison of the resonance positions of the C-7 protons (narrow multiplets, half width about 7 Hz) and of the C-11 protons (triplets, J about 6.5 Hz). It is well established (3) that in 5-substituted 1,3-dioxanes equatorial CH<sub>3</sub> groups as well as the CH<sub>2</sub> protons of ethyl groups are resonating more than half a ppm upfield to the corresponding axial groups. This shift difference is also observed here being 0.76 ppm for the C-7 protons and 0.64 ppm for the C-11 protons, which provides an unambiguous assignment of the diastereomers.

In the case of the parent compound I, R=H, the dioxane moiety is no longer anancomeric (4) and the two ismers now are conformers which are interconverted by inversion of the dioxane ring. Thus, averaged shifts are observed for the protons of the dioxane as well as of the cyclohexene moiety ( $C^{7}H_{2}$ : 1.96 ppm;  $C^{11}H_{2}$ : 1.56 ppm, triplet, J = 6.2 Hz).

I like to conclude by mentioning the fragrant properties of the two isomers IIa and IIb. Although their molecular shape is similar,



they are smelling very differently. Thus IIa smells pleasantly with a note of jasmin and banana, whereas isomer IIb has a muffy odour.

Yours sincerely,

Stor flaget

Alois Steigel

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DEPARTMENT OF PHYSICAL CHEMISTRY ÅBO AKADEMI FINLAND

July 31, 1978

Professor B.L. Shapiro Department of Chemistry Texas A and M University College Station, Texas 77843 U.S.A.

Dear Professor Shapiro,

## Support for the Hybridization Picture of Spin-Spin Coupling

In order to calculate spin-spin coupling constants in molecules one needs the excited, or intermediate, electronic states. Constructing these states has, however, been a problem. Virtual orbitals have been used but they often lead to unstable results.

We have recently found an expensive and approximate, but numerically quite stable method, the Scanning Molecular Orbital (SMO) approach. In this method the set of virtual orbitals is replaced by one, continuously changing orbital with a concomitant density-of-states. The independent variable is the orbital exponent  $\alpha$  of the SMO AD:s <sup>1</sup>. These calculations belong to the *ab initio* variety and do not involve any adjustable parameters.

We have recently applied this method on the  $^{1}$ J(C-C) in C<sub>2</sub>H<sub>n</sub>, (n=2,4,6). The agreement with experiment is fairly good and makes a study of the hybridization interesting:

Molecule	<sup>1</sup> .K (.1.0 <sup>19</sup> m	<sup>1</sup> K (.1.0 <sup>19</sup> m <sup>-2</sup> kg .s. <sup>-2</sup> A <sup>-2</sup> )				
	. Exp.					
C <sub>2</sub> H <sub>2</sub>	226	196				
$C_2H_4$	89	71				
C <sub>2</sub> H <sub>6</sub>	46	26				

The spectral density curve  $\Phi(\alpha)$  consists of a single maximum for each of the three molecules. This single peak in our calculation is built up from four contributions, involving two occupied MO:s ( $\phi_{\mu}$  and  $\phi_{\mu}$ ) and two unoccupied SMO:s ( $\phi_{\mu}$  and  $\phi_{\mu}$ ). The excitation energy values at the peak maximum are comparable for all the three molecules and for all the four excitations ( $\Delta E \cong 1.6 a.u.$ ).

239-42



As seen from the table, this total contribution shows the behavior expected from the traditional hybridization picture. The only difference is that we now have a rather larger excitation energy and spin density instead of those traditionally used.

For the  ${}^{1}K(Si-Si)$  in Si<sub>4</sub> we get a value of  $69 \cdot 10^{19}$ . The extrapolated value of K.G. Sharp et al.<sup>2</sup> is about (84 to 95)  $\cdot 10^{19}$ . We are not aware of any direct measurements.

Herman B. Jansen<sup>§</sup>

Sincerely yours, Pekka Pyylib

Pekka Pyykkö

<sup>§</sup> Department of Chemistry, Free University, Amsterdam

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- K.G. Sharp, P.A. Sutor, E.A. Williams, J.D. Cargioli, T.C. Farrar and K. Ishibitsu, J.Am.Chem.Soc. 98(1976)1977.

## UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19174

Department of Chemistry

July 11, 1978

Dr. Bernard L. Shapiro Texas A&M University NMR Newsletter Department of Chemistry Texas A&M University College Station, Texas 77843

VECTOR IMPEDANCE METER OPERATION AT HIGH FREQUENCIES; POSTDOCTORAL POSITION

Dear Dr. Shapiro:

The first piece of equipment obtained in this NMR laboratory as well as many others that do extensive building of radiofrequency components was a Hewlett-Packard model 4815A RF vector impedance meter. This device is relied on for tuning and matching of NMR probes as well as circuits of other components such as amplifiers and filters. The major limitation of the impedance meter is that its upper frequency is 108 MHz and many nuclei have resonance frequencies significantly higher at magnetic fields commonly in use. This limitation on laboratory tuning capability is so restrictive that there is a story, perhaps apocryphal, that a spectrometer built using a relatively high field solenoid was run at a field low enough for protons to resonate at slightly less than 108 MHz in order to stay in the range of the vector impedance meter. Alternatives to this device include vector voltmeters that do go to high frequencies but are much more difficult to use or far more complex and expensive computer based equipment.

In spite of what a number of members of Hewlett-Packard's engineering and service staffs say, the 4815A impedance meter can be used reliably up to about 250 MHz without modification by merely using an external frequency source. The phase and magnitude adjustments are fully correcting with front panel calibration. We use a commercial doubler (Anzac D1-4) preceded by a 10 db gain amplifier (Anzac AM102) to double the frequency of the internal oscillator of the instrument and then feed this higher frequency back into the instrument. Since all of these frequencies are on external rear panel BNC connectors the unit can be used by itself for applications up to about 218 MHz. Higher frequencies can be obtained with an external synthesizer; around 250 MHz operation starts to become unstable and seems to be a strong function of input signal level and signal purity. Below about 250 MHz operation of the impedance meter is normal as long as the front panel frequency range control is in its highest position and there is sufficient level of input reference signal, hence our use of a small amplifier to make up for losses in the doubler and nonlinearity in the frequency response of the internal oscillator.

A postdoctoral position is available in this laboratory in the areas of NMR spectrometer development or biological NMR. Interested candidates should write directly to S. J. Opella.

Joseph DiVerdi

Busch Graduate Fellow

incerely, Stanley J.

Assistant Professor

## MONASH UNIVERSITY

TELEGRAMS. MONASHUNI, MELBOURNE

CLAYTON, VICTORIA, 3168 FACULTY OF SCIENCE Department of Chemistry. TELEPHONE:

OUR REF.

YOUR REF.

Professor Bernard L. Shapiro, Department of Chemistry, Texas A & M University, College of Science, College Station, Texas, 77843, U.S.A.

Dear Professor Shapiro,

Monash subscription.

## Residual Fine Structure in <sup>13</sup>C Off-Resonance Decoupled

## Spectra

We recently recorded the <sup>13</sup>C spectra of a number of hydroxymethylene cyclohexanones using our Bruker WH90. The chemical shifts observed were as expected on the basis of time-averaging of the enolic forms (I) and (II).



The off-resonance decoupled spectra were also recorded and, as usual, we employed conditions (CW irradiation, 2 watt, centred at 600 Hz upfield of TMS) which normally remove all small  $^{13}C^{-1}H$  couplings and reduce the larger ones to manageable proportions. We therefore were surprised to find that in each case the signal for the quaternary carbon (C<sup>\*</sup>) showed residual splitting of ca. 8Hz. Using gated decoupling the splitting was ca. 13Hz.

Further investigation has traced the trouble to two-bond coupling between the carbon in question and the pseudo-formyl proton (H<sup>\*</sup>). This coupling is only weak but is nevertheless not completely removed under the operating conditions specified because the proton absorbs at relatively low field ( $\delta$  8.6). In order to completely remove the coupling it was necessary to make a substantial change in the decoupling frequency.

Please credit this contribution to Mike Heffernan's

Yours sincerely,

Smiddleta

Sout kao

S. Middleton

I.D. Rae



## UNIVERSITY OF DENVER

An Independent University

University Park, Denver, Colorado 80208

Department of Chemistry / 303 · 753 · 2436

Professor Bernard L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843 July 25, 1978

Correlation Spectroscopy of Exchange Broadened Spectra

Dear Barry:

In many of our dynamic nmr studies we have more than one set of nonequivalent protons which are averaged by the exchange process. In the case of phenyl ring rotation in metallotetraphenylporphyrins (1,2) the chemical shift difference between the nonequivalent meta protons is generally much smaller (1/2 to 1/6) than the chemical shift difference for the ortho protons. Thus the meta protons give sharp fully averaged signals over much of the temperature range where the ortho signals are exchange broadened. Since the ortho and meta signals come quite close together even at 100 MHz we have to work with partially overlapping broad and sharp signals. In many cases the signal to noise ratio is low due to the limited solubilities of the compounds. We were interested in using correlation spectroscopy to improve signal to noise but were concerned about the success of the technique since the broadened signals certainly do not have the Lorentzian lineshape assumed in the correlation. (If the sharp signals hadn't been present we could have just scanned quickly and averaged, but there was too much overlap to exclude the sharp lines from the spectrum.) We could find nothing in the literature, either experimental or calculational, that provides guidance for this situation. A Correlation Spectroscopy Unit was loaned by Nicolet Instruments and attached to our HA-100 by Frank Contratto. We took variable temperature spectra of titanyl tetrakis (p-trifluoromethylphenyl) porphyrin and compared the spectra with the usual c.w. spectra. Over the full range of temperatures from slow to fast exchange we could detect no difference in lineshape between the c.w. and correlation spectra, though the S/N ratio was significantly improved in the latter. The comparison is not perfect since the computer defied all of our attempts to delete the "auto-slow" feature in the plotting routine, making plot widths dependent on noise level. In spite of this minor difficulty (which Nicolet could have solved if we had funds to buy the system ... ) it would appear that correlation spectroscopy works well even for exchange broadened lines with  $\Delta v \sim 30$  hz.

Singgrely,

iseth R. Eaton

Gareth R. Eaton Associate Professor University of Denver

Sandy

Sandra S. Eaton Assistant Professor University of Colorado at Denver

S. S. Eaton and G. R. Eaton, J. Am. Chem. Soc. <u>99</u>, 6594 (1977).
 S. S. Eaton, D. M. Fishwild, and G. R. Eaton, <u>Inorg. Chem.</u> <u>17</u>, 1542 (1978).

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